Preface

Organic conjugated systems are attractive because of wide range of applications, which includes stimulated emission from π-conjugated polymers, optical switches, organic solar cells and organic light emitting diodes, to name a few. They have the advantage of low cost, ease of processing and tunability of their linear and nonlinear optical properties by functionalization with donor or acceptor groups.

In chapter 1, we provide an introduction to the π-conjugated systems and various interesting phenomena observed in these systems, This is followed by a brief description of the application of the above mentioned π-conjugated systems for organic light emitting diodes, and organic photovoltaic cells. In the last section of this chapter, we give an introduction to magnetism due to π-electron systems.

In chapter 2, we begin with energy band theory in one-dimension and its drawbacks. We introduce various model Hamiltonians which incorporate electron-electron interactions like Hubbard model, and Pariser-Parr-Pople (PPP) model. We present numerical techniques like valence-bond (VB) and constant M_S techniques that are used to exactly solve the above model Hamiltonian. This is followed by an introduction to density matrix renormalization group method (DMRG) employed for the above model Hamiltonian for larger system in one-dimension and quasi-one-dimension. We give description of linear and nonlinear optical properties followed by the oriented gas model for ensemble of molecules. Various methods for computing polarizabilities and hyperpolarizibilities of molecules includes such as Finite-Field method, Sum-Over-State Method, and Correction Vector (CV) Methods are described in detail.

In chapter 3, we look into fused azulene systems as a possible organic multiferroics. Azulene molecule with fused five and seven membered π-conjugated rings has a dipole moment, and the π-framework has geometric frustration. Hence in fused azulenes we can expect both ferroelectric and magnetic ground state. To explore this, we study low-lying correlated electronic states of fused azulenes using the long-range interacting PPP model and the finite DMRG method. The ground state is a singlet for oligomers up to 5 azulene units. For oligomers with more than 5 azulene units and up to 11 azulene units the oligomers have a triplet ground state. From the excitation gaps between the lowest $M_S = 0$ state and the lowest states in M_S=1, 2, and 3 sectors we predict that the ground-state spin of the fused azulene increases with the number of azulene units. In the thermodynamic limit, we expect the fused azulene

to be a ferromagnet. Charge density calculations show that the ground state of the system has ferroelectric alignment of the dipoles of the monomeric units. Thus, a fused azulene system could be the first example of an organic molecule which is both ferromagnetic and ferroelectric, in the ground state.

In chapter 4, we study the linear and nonlinear optical properties of diradical systems. We have studied linear and non-linear optical properties of π-conjugated diradicals because they are expected to exhibit large non-linear responses. The system studied are oligomers of dicyclopenta-fused acenes (DPA) and the s-indaceno[1,2,3-cd;5,6,7-c'd']diphenalene (IDPL) molecule. Spin-spin correlation functions within a correlated PPP model Hamiltonian, using exact diagonalization method, are used to characterize the diradical nature of DPA-2 and similar calculations on Anthracene have been performed to contrast this with a singlet character. The diradical character of DPA-2 is also manifest as low optical gap, low spin gap and large THG coefficients compared to Anthracene molecule. Larger DPA-k, k $>$ 2, oligomers as well as the IDPL molecule have been studied within the DMRG technique. In the DPA-4, we find a very small spin gap (0.04 eV), while in the oligomers with k $>$ 4, we find that the ground state is degenerate with the lowest triplet state. The energy of the second excited triplet state decreases with increasing size k and seems to saturate at $\sim$ 0.36 eV in the thermodynamic limit. The lowest optical gap in DPA-4 is at 1.94 eV and has large transition dipoles, while for DPA-k, 4 $<$ k $\leq$ 28, we have not been able to access states with large transition dipoles. The weak low-energy excitations seem to saturate at 0.5 eV and the two-photon gap also seems to be saturating at $\sim$ 0.3 eV in the thermodynamic limit. These polymers will not be IR fluorescent by Kasha rule. The dominant component of the THG coefficient, γ_{xxxx}, is highest for DPA-4 which reduces almost by an order of magnitude in DPA-8; for k $>$ 8 it increases up to the largest system with k=20 for which we have computed the coefficient. The variation of the charge gap of DPA oligomer with the increase in system size is small and in the polymer limit the charge gap is 4.24 eV. For IDPL molecule spin gap is 0.20 eV and next excited triplet state is at 1.48 eV. Two lowest singlet states in B space are nearly degenerate and have large transition dipole moments. Optical gaps to the above states are 2.20 eV and 2.22 eV. Two-photon gap in this system is 1.29 eV, hence this system is also non-fluorescent. We calculated the dispersion of the major component of the THG coefficient, γ_{xxxx}, over a wide frequency range for this molecule, and we observe resonances corresponding to the 2^1A_g and 1^1B_u states. Extrapolated value of γ_{xxxx} at zero frequency is 15.58 x 10^6 a.u which is very large

and the system does not have any donor or acceptor substituent groups.

In chapter 5, we study absorption spectra and two photon absorption coefficient of expanded porphyrins (EPs). We find that in the 4n+2 EPs there are two prominent low-lying one-photon excitations while in 4n systems there is only one such excitation. The two-photon gaps in both these types of systems are at energies close to the one-photon excitations. The spin gap in 4n+2 EPs are very small although the spin-1/2 Heisenberg calculations show that a pure spin system in this geometry will not have vanishing spin-gap. The charge density rearrangement in the one-photon excited state is most at the aza nitrogen site and at the meso carbon sites. In the two-photon states also the charge density rearrangement occurs mostly at the aza-ring sites. The bond order changes in these states is much more striking. In the one-photon state, the C-C bond length in the aza rings show a tendency to become uniform. Similar qualitative trend is also observed for the two-photon state.

In chapter 6, we study linear and nonlinear optical properties of two push-pull polyenes stacked in head to head (HtH) and head to tail configurations (HtT), at different stacking angles, exactly within the PPP model. Varying the stacking angle between polyenes, we find that the optical gap varies slightly, but transition dipoles show large variation. The dominant component of first-order hyperpolarizability, β_{XXX} for HtH and β_{YYY} for HtT arrangement strongly depend on the distance between molecules. The β_{XXX} for HtH configuration shows a maximum at a nonzero stacking angle, which varies with inter polyene distance. ZINDO study on two monomers, (4-hydroxy-4′-nitro-azobenzene) connected by a conjugated bridge shows that β_{av} is more than twice the monomer value and with a red-shift in the optical gap.

In chapter 7, we have calculated the shifts in optical gaps and band edges as a function of the distance between two monomers within a correlated PPP model Hamiltonian for various stacking geometries. We have used as model monomers, both unsubstituted polyenes and push-pull substituted polyenes. We have carried out calculations with and without inter-chain hopping between sites on different molecules. We note that in the absence of inter-chain hopping, the energy level shifts are almost independent of the distances between the chains in all stacking geometries. It is also interesting to note that only electron-electron interactions yield a blue shift in the optical gaps for parallel stacking, but red shift in the gap for all other stacking geometries. We note that most of the shift in the gap is due to shifts in the excited

state energy and the ground-state energy remains almost the same. With interchain transfer the shift in the optical gap increases with decrease in the interchain distance. We observe red-shifts in parallel stacking geometry when inter-chain electron hopping is turned on, at small interchain separations. In general interchain hopping increases significantly the red shift in the optical gaps for all geometries. Even for push-pull polyenes of $|\epsilon|$=2.0 eV, we observe the same trend in the shift in the optical gap for various stacking geometries. In this case the shift in optical gap is an order of magnitude higher when interchain hopping is turned on compared to that in the absence of interchain hopping. We find that the optical gap shifts are largest for the parallel stacking geometry, and it also shows stronger distance dependence. This is in close conformity with experimental observation of red-shift in absorption maxima when hydrostatic pressure is applied on the system. The shift in the HOMO (LUMO) level is small in the absence of $t_\perp$, and the largest shift is in the case of parallel stacking compared to other stacking geometries. The distance dependence of the HOMO shifts is also rather weak. When $t_\perp$ is turned on, the level shifts become large by a factor of five or more. When we have push-pull groups electron-hole symmetry is broken and the shift is different for the HOMO and the LUMO level. Depending upon stacking geometry, the HOMO shifts vary from $\sim$ 0.1 eV to 0.3 eV, which is larger than the shifts observed in unsubstituted polyenes. This large shift in the LUMO reduces the efficiency of exciton dissociation.